

WO 97/41403

PCT/EP97/02104

Ignition Mixtures

The present invention relates to ignition mixtures and manufacture and use thereof.

Ignition mixtures and primers are used to ignite pyrotechnic mixtures or primers as well as propellant charges. The pyrotechnic mixtures or primers can represent the single charge or a booster charge or a gas-generating primer. Propellant charges and primers convert into primarily gaseous components which can be used to trigger rapid-acting processes such as acceleration of projectiles, driving in fastening materials, for example with the aid of bolt setters, or inflating air bags or triggering belt tighteners in vehicle safety. One variant is represented by the use of liquid primers instead of solid primers. These exploit the reaction of liquid fuel with oxidizers to generate gases.

Ignition mixtures are generally triggered mechanically so that they must be sensitive to the action of friction and impact. They generally consist of initial or primary explosives such as lead trinitroresorcinate or diazodinitrophenol, reducing agents such as metal powder, or oxidizers such as barium nitrate or zinc peroxide. Sensitizers such as tetrazene or friction agents such as powdered glass, which increase the sensitivity of the initial explosive materials, are also used. For electrically ignitable systems, the rapid-reacting initial explosives are primarily used. However, the high mechanical sensitivity of the components required for perfect function is a disadvantage when handling the raw materials and mixtures. Handling requires special safety measures. Other types of ignition such as ignition by heat or by coupling high-frequency electromagnetic waves do not solve this problem or are suitable only for highly specialized and sharply limited applications.

The goal of the present invention is to provide new ignition mixtures.

In a first embodiment of the invention, the problem is solved by ignition mixtures that can be ignited by laser light. The explosives contained in the ignition mixtures according to the invention can be primary or initial explosives, secondary explosives, or mixtures of these explosives. The primary or initial explosives that can be used may for example be lead

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trinitroresorcinat, diazodinitrophenol, tetrazene, or potassium dinitrobenzofuroxanate, or mixtures of these explosives. Appropriate secondary explosives are chosen from nitrocellulose, hexanitrostilbene, nitrated aromatic compounds, and/or nitrated aromatic compounds with a polymer structure such as polynitropolyphenylether or polynitropolyphenylenes, from specific heterocycles such as nitrotriazolone, from the derivatives of tetrazoles such as aminotetrazole, ditetrazole, or diaminoguanidine azotetrazole, and from hexagene or octagene. Secondary explosives derived from urea and its derivatives can also be used. Examples of these are the urea derivatives biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, thiourea, triaminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, tetrazene, semicarbazide nitrate, as well as urethanes, ureides such as barbituric acid, and their derivatives. These explosives can be used alone or in a mixture. According to the invention, secondary explosives are preferred, and nitrated aromatic compounds with a polymer structure, in particular polynitropolyphenylether and the polynitropolyphenylenes or mixtures of these secondary explosives are particularly preferred.

In addition to the explosives, the igniters according to the invention also contain oxidizers and reducing agents which are common per se. Binders, processing agents, and pressing agents can also be used.

Oxidizers that may be used can be the peroxides of alkali metals and alkaline earth metals, zinc peroxide, and the peroxodisulfates of the aforesaid elements and of ammonium, nitrates of alkali metals, and alkaline earth metals, in particular lithium, sodium, potassium, or strontium nitrate, as well as ammonium nitrate, oxohalogen compounds of alkali metals or alkaline earth metals or of ammonium, and particularly preferably potassium perchlorate or ammonium perchlorate. Sulfur is also suitable as an oxidizer. These oxidizers can be used alone or in a mixture.

The reducing agents used according to the invention are metals such as titanium, zirconium, aluminum, magnesium, and cerium in the finely powdered form. Alloys of these metals as well such as titanium/aluminum or cerium/magnesium can be used according to the invention. Other reducing agents are carbon or boron. These reducing agents can be used alone or in a mixture.

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Compounds from the group of polyesters or polyurethanes can be used as binders. Compounds with binding properties that contribute to the heat of explosion and/or the oxygen balance, for example nitrocellulose or polynitropolyphenylene, can also be used as binders.

Processing agents and pressing agents can be substances which for example improve flowability such as Aerosil or substances which impede dust formation and improve slip or meterability, such as graphite or boron nitride.

For improved absorption of laser light, the ignition mixtures according to the invention can also be dyed or reacted with dye pigments. Heat stability can also be improved if necessary by adding stabilizers. Substances used to stabilize nitrocellulose can for example be used for this purpose.

In addition, combustion moderates that affect the rate of combustion can be added to the ignition mixtures according to the invention.

Substances or mixtures thereof able to affect combustion and combustion rate by heterogenous or homogenous catalysis are used as combustion moderates. Moderator that participate in the reaction in the form of heterogenous catalysis are metals, metal oxides, and/or metal carbonates and/or metal sulfides. The metals that can preferably be used are boron, silicon, copper, iron, titanium, zinc, or molybdenum. Calcium carbonate can also be used. Mixtures of these moderators can also be used.

Moderators that react in the form of homogenous catalysis are for example sulfur, copper resoricates, or ferrocene and its derivatives. These moderators are evaporated by the temperatures produced by the reaction and can thus affect the reaction themselves or as secondary products.

For protection against environmental influences, the ignition mixtures according to the invention can also be treated with protective agents or be coated.

The ignition mixtures according to the invention have multiple potential uses. For example, they are used to ignite pyrotechnic mixtures or primers as well as propellant charges that trigger rapid processes such as acceleration of projectiles, driving in fastening materials, for example with the aid of bolt setters, or inflating air bags or triggering belt tighteners in vehicle safety.

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The safety data on some of the ignition mixtures according to the invention are provided in Table 2. The data were derived by the methods of the Bundesanstalt für Materialprüfung [Federal Institute for Materials Testing]. By comparison to the primary explosive lead nitroresorcinate, sensitivity to friction and impact are significantly improved with the igniting agents according to the invention.

In estimating important parameters of the ignition mixtures according to the invention such as the energy released by the reaction (heat of explosion), pressure, explosion temperature, and reaction products produced at this temperature, an adiabatic reaction was calculated with a thermodynamic computer program for the ignition mixtures according to the invention at constant volume and a loading density of 0.1 g/cm^3 . Table 3 shows the most important data in the thermodynamic calculation. The ignition energy necessary for triggering a reaction was determined experimentally.

The examples below are intended to illustrate the invention without restricting it.

Examples 1 to 16:

The ignition mixtures according to the invention were produced by methods known of themselves. The individual components were sifted through a sieve with a small mesh size of 0.2 mm as shown in Table 1 and mixed in a tumble mixer for 30 minutes. 200 mg portions of these mixtures were pressed into pellets with a diameter of 6 mm with a pressing force of 71 N/mm^2 . The pellets so produced were ignited with a laser beam (wavelength 1,060 nm) with an energy of approximately 200 mJ and a pulse length of 2.5 ms. The ignition behavior is shown in Table 1

Table 1

Examples																
Components	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
KNO ₃	52.5	52.5					33.3	32.3				33.3	40			40
B	18.8	18.8						2.9		2.9			10			10
binder	3.7	3.7														
NPE	25		45	44.7	44.5	44.1	66.7	64.8	66.7	64.8				25	25	50
PNP		25									100	66.7	50			
ZnO ₂			50	49.8	49.8	49				33.3	32.3					
Ti			5	4.9	4.9	4.9										
graphite				0.5	1	2								75	75	
black powder																
ignition behavior	+++	+	+	+	+	+	+	++	+	+	+	+++	+++	+	+	+++

+ = ignition
 ++ = good ignition
 +++ = very good ignition

Components Used:

KNO₃ potassium nitrate < 200 μm
 B amorphous boron
 Ti titanium metal powder < 40 μm
 binder polyurethane

NPE polynitropolyphenylether
 PNP polynitropolyphenylene
 ZnO₂ zinc peroxide, mean grain size 6.5 μ, oxygen content 13.5%

Table 2

Specimen	Pressure (atm)	T (K)	Ex. Heat (cal/g)	Condensate Percentage (%/mol)	Ignition Energy (mJ)
NPE	1109	2932	686	0	≈ 10
NPE/KNO ₃ 66.7/33.3	907.4	3073.5	672	7.5	160
NPE/ZnO ₂ Ti 45/50/5	1198	4146	978	14.6	≈ 200
black powder/NPE 75/25	430	2290	-179	11.6	≈ 200
AZM O 9531/NPE 75/25	622	3265	615	52	≈ 200
NPE/KNO ₃ /B 50/40/10	843	3374	673	29	≈ 90
NPE/ZnO ₂ 66.7/33.3	1341	4044	1016	7	> 200
NPE/ZnO ₂ /B 64.8/32.3/2.9	1194	3731	991	14	> 200
NPE/KNO ₃ /B 64.8/32.3/2.9	1002	3382	752	2	≈ 100
NC/KNO ₃ 66.7/33.3	872	3282	883	11	no ignition
lead trinitroresorcinate	683	3639	550	10	≈ 5

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Table 3

Explosive	Friction Sensitivity (N)	Impact Sensitivity (J)	Detonation Point (°C)
lead trinitroresor- cinate	2	≤ 0.025	280
AZM O 2956	≥ 360	5	> 400
AZM O 9531	≥ 360	4	> 400
black powder	≥ 360	5	> 400
HITP (aminotetrazole base)	≥ 360	15-50	> 400
NPE	≥ 360	7.5	> 260
NPE/ ZnO_2 /Ti	≥ 360	15	230
NPE/ ZnO_2	240	20	235
NPE/ KNO_3 + 3% B	160	4	decomposition starting at 230
PNP/ KNO_3	≥ 360	10	293
PNP/ KNO_3 /B	≥ 360	10	293

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